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STUDIES ON THE MAGNETIC SUSCEPTIBILITY OF THE Cr^{+3} ALUMS IN THE RANGE 300°K to 100°K.

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ABSTRACT The results of some accurate measurements of the magnetic susceptibility of a series of Cr^{+3} double sulphate, sulphato-selenate and selenate alums in the range 300°K to 100°K have been discussed in the present paper. Analysis of the mean square moments shows the existence of an appreciable contribution from Van Vleck's high frequency paramagnetism and an orbital contribution to the Curie term comparable to the high frequency term, over and above the spin contribution. The Weiss term due to spin separation by the anisotropic crystalline field, is, however, negligibly small in the Cr^{+3} alums in our temperature range. In most of the alums an appreciable temperature dependence of the h.f. and Curie term is observed, stimulating the effect of a Weiss term. This temperature dependence is reversible and may be better represented by two sets of h.f. and Curie coefficients, one for upper and the other for the lower range of temperature, and evidently arises from the thermal expansion of the alum lattice and very probably also from the variation with temperature in the proportion of the two coexisting phases of the α, β and γ alums or the thermal conversion from one phase to another, and the consequent changes in the crystalline electric field acting on the Cr^{+3} ion.

Taking the spin orbit coupling to be not very different from the free ion value of $+87$ cm^{-1}, optical absorption and paramagnetic resonance results have been compared with the magnetic susceptibility data and an estimate of the covalency factor and cubic separation of the orbital levels made.

INTRODUCTION

The magnetic behaviours of chromium alums are apparently very simple. The single crystals of the alums being of the cubic class show no magnetic anisotropy. The mean susceptibility of the Cr^{+3} alums has been found to obey very closely a Curie law of temperature variation (de Haas and Gorter, 1930; Serres, 1932), with a value of the magnetic moment very nearly equal to the "spin only" value, which has made the alums eminently suitable for the production of extremely low temperatures by the method of adiabatic demagnetisation (de Klerk, Steen-land and Gorter, 1949). But a limit is set to the low temperature obtained, by a small twofold splitting of the spin levels of the Cr^{+3} ion, evidently caused by a small departure from cubic symmetry of the crystalline electric fields in the alums. This also should cause a slight departure of the susceptibility from the Curie law, and a small anisotropy of the Cr^{+3} ion.

The Cr^{+3} alums have been recently the subject of extensive investigations by the paramagnetic resonance method (Bleaney *et al*, 1951), which directly gives the value of the spin splittings of the individual Cr^{+3} ion. But the optical absorption spectra do not show any level corresponding to the splitting of the orbital levels by the anisotropic field. Also several anomalies and uncertainities have been observed at low temperatures in the paramagnetic resonance observation, the causes of which are not very clear. The structural data also indicate that in some of the alums at least the Cr^{+3} ions are under the influence of a non-cubic crystalline electric field due to the surrounding charges and dipoles.

We have therefore undertaken an extensive series of accurate measurements of the susceptibility of a large number of Cr^{+3} alums, between the range 300°K to 100°K, expecting to throw more light upon these problems, the results of which are discussed in the present paper.

DETAILS OF THE EXPERIMENTAL METHOD

(*a*) *Preparation of the sample*:

The chromium alums have the general formula, $Cr\ A(XY_4)_2,\ 12H_2O$, where $A = K$, NH_4, Rb, Tl, Cs, NH_2OH etc. and $(XY_4)_2 = (SO_4)_2$, $(SeO_4)_2$ or $(SO_4)(SeO_4)$. They crystallize commonly in the form of deep violet octahedra and are in many cases easily obtainable as large single crystals by the slow evaporation of a nearly saturated aqueous solution of the component salts in equimolecular proportion. For example, in the case of sulphates and sulphato-selenates the corresponding component salts (of analytical quality of Kahlbaum, Merck or Malinckrodt) are dissolved in double distilled water, crystallized several times to purify them and finally crystallized in a quiet dust free and vibration-proof chamber by moderately slow evaporation of the nearly saturated solution, kept in flat-bottom crystallizing dishes. The temperature of the chamber is not allowed to fluctuate much during crystallization, by suitable lagging of the chamber. In several cases the component salts were prepared by ourselves using analytical quality of the hydroxides or carbonates of the metals and the desired acids. The analytical purity of the final materials were always carefully checked. It was found in some cases that while exposed to air for free evaporation for sometime, particularly if the room temperature remained above about 30°C, as happens during the hot weather, the aqueous solution turned green, no doubt due to formation of complexes by the Cr^{+3} ion, with the anions. Even then, in some cases the crystals came out as violet octahedra as usual. But in such cases there is some likelihood of contamination of the alum by the green complex. We have therefore taken precaution not to use crystals out of such crops. We have prevented such occurences in future by putting the dishes of the solutions to be crystallized in a vaccum desiccator with a suitable desiccant and the whole thing within a double walled ice-box, in which the temperature

may be maintained at 20°C by putting in it a suitable amount of ice, replenishing it as necessary.

The tendency for the green complex formation in the alums is so marked in the sodium sulphate alum, that the solution even from the moment of preparation was dark green and inspite of many trials became treacly on evaporation and never crystallized, but dried up into a green conglomerate mass. The same tendency is also very marked in the selenate alums in general and we could prepare only two of them (NH_4 and Rb alums) adopting a somewhat different technique. About 4.000 grams of $Cr(NO_3)_3$ and 3.582 grms of $(NH_4)_2SeO_4$ (or Rb_2SeO_4 as the case may be) are separately dissolved in ice cold double distilled water and the two solutions are mixed together keeping the mixture always below 5°C using an ice bath and with constant stirring. Precooled acetic acid is added drop by drop and the alum is precipitated as fine shower of violet microcrystals. The precipitate is washed with acetone to free it from acetic acid and is again dissolved in double distilled water and reprecipitated with acetone, all the processes being carried out at low temperature. The purified precipitate is again dissolved in ice cold water and left for crystallization in the ice-box controlling its temperature below 5°C, with large blocks of ice. Large violet octahedral crystals thus obtained are once again crystallized in the same manner for use in magnetic measurements.

The best of the crystals free from distortion and of as nearly possible symmetric shape were chosen from each crop, firstly with a magnifying glass and then under a polarising microscope, stored in a dry clean test tube (stopper of which is sealed with wax) and indexed. But in several cases where the crystals have a tendency to dehydrate, melt or decompose quickly, the sample on removal from the mother liquor and cleaning, is coated with an extremely thin layer of collodion or durofix by momentarily dipping it in a dilute solution of these substances and immediately used for magnetic measurements.

(*b*) *Method of Magnetic Measurements*

As we have already mentioned alums being of the cubic class, the magnetic measurement consists only in finding the mean susceptibility of the crystals at different temperatures. For this reason our information about the magnetic behaviour of Cr^{+3} ion derived from such measurements are necessarily more limited, than could be obtained from those on crystals of lower than cubic symmetry, e.g the hydrated salts of Cu^{+2} and Ni^{+2} ions (Bose, Mitra and Datta, in course of publlication). It has been pointed out however, that the effect of the anisotropic crystalline electric field may vary from alum to alum and thus manifest itself even in the mean susceptibility (Bose and Mitra, 1952), when refined techniques of measurement are adopted for a large number of these salts. The mean susceptibility might have been obtained by using the powdered crystals in glass ampoules, but apart from the tediousness of the process of packing of the powder in the

ampules, errors are likely to arise due to uncertainity in the density of packing. A further drawback is that while finely powdering and packing, most of the crystals, which are highly hydrated, are found to loose some water or decompose. So we have preferred to use single crystals of suitable size. They are also chosen to be of very regular shape to avoid errors due to demagnetizing coefficient. A trial with different shapes of crystals not very much departing from an octahedron or cube, was carried out in this laboratory to observe this effect which was found to be not more than 1 part in 1000 even at 100°K (Datta, 1954). Since the crystals of the alums are isotropic, it is not necessary to set them in the field in any preferred direction of orientation.

A refined Curie balance and a liquid air cryostat are used for the measurements, firstly to find out accurately the values of the absolute susceptibility of the crystals at room temperature (300°K) by comparison with a chrome potassium alum crystal standardised against a standard $NiCl_2$ solution. Magnetic forces on the sample, mounted at the end of the horizontal balance arm, placed in a *vertical* magnetic field with a *horizontol* gradient, is balanced accurately by twisting the vertical quartz fibre from which the balance beam is suspended. The forces at the other constant temperatures down to 100°K, are then compared with that at room temperature, retaining all other conditions e.g. suspension, magnetic field etc, the same as at room temperature. The details of the balance and the cryostat, the method of measurement and avoiding or correcting the various errors, are fully discussed in an earlier paper by the author (1955) and need not be repeated here. Some remarks, however, should be made here about the probable limits of error in the present measurements and the final treatment of the results of observation for the purpose of discussion.

As is indicated in our earlier paper the overall error in the susceptibility measurement at room temperature is about 0.2 % including the unce rtainty of temperature measurement and slight differences in the value for different crystals, to reduce which the mean value for 3 or 4 such crystals is taken. With the fall of temperature the susceptibility increases and the accuracy of measurement increases. The values at low temperatures relative to that at room temperature have even greater accuracy, of about 0.1 %, since all other conditions of the experiment remain practically the same, though this is somewhat offset by the slightly increased inaccuracy in temperature measurement. There is a chance that during a series of measurements a crystal might undergo some permanent change physically or chemically. To detect this effect, two series of measurements with the same crystal *in situ* were carried out, one going from room temperature down to the lowest and the other back again. In case of any irreversible changes occurring, two such susceptibility curves would be more or less different. We could not observe any such appreciable difference, (except in the case of ammonium selenate alum), which shows that in our conditions of measurements most of these alums are more or less stable, particularly when most of the time

they are kept below room temperature. As we have noted, several of the crystals slowly tend to dehydrate or decompose at or above about 300°K, to avoid which we had to start low temperature measurement very soon after preparation. Again in one or two cases in e.g., K and NH_4 sulphate alums, we had observed slow surface dehydration occurring on prolonged exposure to the dry air of the experimental chamber at liquid air temperature. In the NH_4 selenate alum similarly a slight melting of the crystal was observed after the run back to the room temperature was completed. A coating of collodion or durofix helped to check these. Our entire series of measurements at low temperature were finished before appreciable change in susceptibility curve could occur. A large number of readings, at the interval of 15° to 20°K or even closer, where thought necessary from a preliminary run, are taken to follow the susceptibility curve very closely, to see whether it contained any changes in slope or any other singularity which may be reversible with temperature. This was found to occur in most of the crystals.

From the temperature variation measurement of the angle of torsion, say α, of the quartz fibre required to balance the sample against the magnetic force, a graph of $\alpha . T$ against absolute temperature T is prepared, which is a line with a small slope against T axis and a small curvature. From this curve intrapolated values of α's may be obtained at 300°K and at other temperatures at 20°K interval down to 100°K. Knowing the susceptibility at 300°K, the values at other temperatures may be calculated from the formula,

$$\frac{F_T}{F_\theta} = \frac{\chi_T}{\chi_\theta}\left[1 + \frac{k_{a\theta}}{k_\theta}(1 - \gamma\theta)\left(1 - \frac{\theta}{T}\right)\right] \quad \ldots (1)$$

where χ_T and χ_θ are the gram-molecular susceptibilities of the crystal at temperature T and 300°K respectively, and F_T and F_θ are the forces acting on the crystal at these temperatures, $k_{a\theta}$ and k_θ are the volume susceptibilities of air and that of the crystal at 300°K, and γ the coefficient of thermal volume expansion of the crystal.

The above method of graphical intrapolation is very sensitive to experimental scatter and we have found that all our points for a given crystal lie on a smooth curve within the limit of our accuracy of about 0.2%. This method of treating the results is also better for our ultimate discussion of the results in terms of the squares of the mean effective moments which are very nearly proportional to $\alpha.T$'s. From the values of the mean gm. molecular susceptibility χ_M (after correcting for diamagnetism of the molecule) thus obtained at different temperatures, the square of the mean effective magnetic moment p_f^2 in Bohr magnetons is calculated from the formula.

$$p_f^2 = \frac{3k\chi_M T}{N\beta^2} = 7.995\chi_M T^*, \quad \ldots (2)$$

in which the other symbols have the usual meanings.

*The latest values of physical constants $k = 1.38032 \times 10^{-16}$ ergs. deg^{-1}, $N = 6.0243 \times 10^{23}$, $= .92731 \times 10^{-20}$ erg. gauss^{-1} (Dumond and Cohen, 1948) are used.

TALBE IX

$Cr_2(SO_4)_3,Rb_2(SeO_4),24\ H_2O$

Temp°K	$\chi_M \times 10^6$	pf^2	
		Obs.	Calc.
300	6125	14.65	14.69
280	6541	14.65	14.65
260	7028	14.61	14.62
240	7598	14.58	14.58
220	8276	14.57	14.57
200	9098	14.55	14.55
180	10120	14.56	14.56
160	11395	14.56	14.56
140	13010	14.55	14.56
120	15175	14.55	14.56
100	18220	14.56	14.56

TABLE X

$Cr_2(SO_4)_3,Cs_2(SeO_4),24\ H_2O$

Temp°K	$\chi_M \times 10^6$	pf^2	
		Obs.	Calc.
300	6116	14.67	14.67
280	6546	14.65	14.65
260	7037	14.62	14.62
240	7611	14.61	14.59
220	8287	14.58	14.57
200	9104	14.55	14.55
180	10093	14.52	14.52
160	11380	14.55	14.57
140	13080	14.63	14.63
120	15250	14.63	14.61
100	18240	14.59	14.59

TABLE XI

$Cr_2(SeO_4)_3,(NH_4)_2,(SeO_4),24\ H_2O$

Temp°K	$\chi_M \times 10^6$	pf^2	
		Obs.	Calc.
300	6050	14.51	14.51
280	647	14.51	14.51
260	6981	14.51	14.51
240	7563	14.51	14.51
220	8255	14.51	14.50
200	9070	14.50	14.50
180	10075	14.50	14.50
160	11369	14.55	14.55
140	13000	14.55	14.55
120	15166	14.55	14.55
110	16555	14.55	14.55
104	17060	14.46	–
100	18064	14.45	–

TABLE XII

$Cr_2(SeO_4)_3,Rb_2\ SeO_4),24\ H_2O$

Temp°K	$\chi_M \times 10^6$	pf^2	
		Obs.	Calc.
300	6141	14.72	14.72
280	6570	14.71	14.71
260	7060	14.70	14.70
240	7650	14.68	14.68
220	8339	14.67	14.67
200	9160	14.66	14.66
180	10180	14.64	14.65
160	11440	14.63	14.63
140	13060	14.62	14.62
120	15220	14.60	14.60
100	18260	14.60	14.60

DISCUSSION OF THE RESULTS

(1) *Variation of the p_f^2 from salt to salt and with temperature.*

It will be seen immediately from the values given in tables, that p_f^2 is in general appreciably different from the 'spin only" value of 15 Bohr magnetons for Cr^{+3} ion and is also different from salt to salt. The values of p_f^2 for NH_4 and Tl sulphate and NH_4 selenate alums are seen to be appreciably smaller than the others. It will be seen further that p_f^2 values do not obey the Curie law very well i.e. are not constant with temperature but go on changing appreciably and in a manner characteristic of the given salt. However, certain general features may be observed. In Rb and Cs sulphate and Rb selenate alums, the values of p_f^2 go on falling more or less systematically with temperature; the values become practically constant below about 140°K. For Rb sulphato-selenate salt there is a small decrease down to about 200°K and then it is very nearly constant. For K sulphate and NH_4 sulphato-selenate the initially falling curves rise up rather quickly between about 200°K-160°K, and 220°K-180°K respectively, and then start falling again. In NH_4 and Tl sulphate and K and Cs sulphato-selenate, the value decreases down to about 220-180°K and then rises more or less slowly except for the last salt which shows a fall again below 140°K. In (NH_2OH) sulphate, the value, being nearly constant down to about 200°K, rises down to 140°K and then starts falling. In NH_4 selenate alum p_f^2 remains practically constant down to 180°K, rises fairly suddenly between this temperatures and 160°K, remains about steady and then sharply falls down below 106°K. Thus it will be seen that in several of the alums a distinct change in the slope of the curve occurs somewhere about the middle of our temperature range, extending over about 20-40 degrees, perhaps even more. *Actually, a similar change in the slope was indicated in the Leiden data of de-Haas and Gorter (1930; see also Dutta Roy, 1955) for K sulphate alum e.g. 14.92 at 290°K, 14.88 at 143.6°K and 14.91 at 77.7°K. However they did not put any significance to this departure from linearity in their curves and smoothed the susceptibility data to accord to the formula,

$$p_f^2 = 14.92 + \frac{1.32}{T} \qquad (3a)$$

On a rigorous analysis of their data it has been found that between 290°K and and 14°K these obey the following formula, much better.

$$p_f^2 = -.0002693T + 14.91 + \frac{1.867}{T} \qquad \ldots \quad (3b)$$

It has been already mentioned that the change in the curvature of the $p_f^2 - T$, curves are generally exactly reversible and reproducible with falling and rising

*In our earlier paper (Dutta Roy, 1955) all the p_f^2 should be reduced by a factor 7.995/8.061 owing to correction for the latest value of physical constant.

temperature, so that they can not be attributed to possible changes in the structures due to decomposition or dehydration as referred to earlier, except in the case of NH_4 selenate alum below 110°K.

To compare our results with the existing theories and to explain the various peculiarities observed, it would be better to try to analyse the data with an empirical three-constant formula of the form,

$$p_f^2 = AT + B + \frac{C}{T} \qquad \ldots \quad (3c)$$

in which the terms are evidently those corresponding to temperature independent, Curie and Weiss terms respectively, in susceptibility. The constants A, B, C, are determined from the experimental data by the method of least squares. It was, however, found that though in several alums such a formula would fit reasonably well with experimental values at both the higher and lower sides of the temperature range, it gave a wide systematic deviation in all the others beyond experimental errors, from the experimental values in the medium temperature range, where singularities are usually observed in the experimental curves. These deviations are such that the addition of T^2 and $1/T^2$ terms though improving the fit with experimental values would unduly complicate the situation. On the other hand, it was found that the observed values on *either side* of the singularity might be made to fit very well with a simple formula of the type $p_f^2 = AT + B$, with different values of the constants (A_1, B_1), (A_2, B_2). The values of p_f^2 calculated back from these two sets of constants are given in Tables (I—XII) side by side with the experimental values for comparison. The horizontal lines in the last column indicate the range of applicability of each formula. One or two values in the intermediate range not fitting with either formula individually, give, however, a farily good fit with a formula with mean A and B values. All this evidently means that in this region the A and B values are changing more or less continuously (of course reversibly) from one set of values to another as the temperature changes. The values of A and B for upper and lower ranges of temperature for the individual salts are given in Table XIII.

It will be seen from this table that A_1 values are small in all cases, their contributions to p_f^2 being not more than about 4 % of the total at room temperature, falling to less than 2 % near the middle of the range. On passing through this region, as A_1 changes to A_2, the contribution of this term at the beginning of the lower range rises again to about 4 % and then decreases again by about the same amount at the bottom of the range in the cases where A_2 is found to be positive. It is obvious, however, that these values may not be correct to more than about 10 to 25 % ; particularly in the cases where calculations are made from the variations of p_f^2, small and confined to only a few temperatures. B-values are correct to about 0.2 % and contribute the bulk of the moment, about 96 %. The significance of A and the leading term B and its variations in the different temperature

ranges and from salt to salt will be discussed more fully in a later section with reference to the structure of the alum and the crystalline field theory.

(*b*) *Structure of the alums.*

All the alums belong to the cubic class of crystals with four molecules in the unit cell. From the analysis of the structures of the alums (Beevers and Lipson, 1935; Lipson, 1935;Klug 1940), it appears that the alums are not strictly isomorphous, and may be divided into three classes α, β, and γ, with reference to the size of the monovalent cation and the differences in the symmetry and orientations of the different groups of atoms in the unit cell. In all the alums the trivalent cation is immediately surrounded by an octahedron of water molecules. In the α-class the water octahedron is found to be slightly distorted along its trigonal axis which lies along a body diagonal of the unit cell, and the octahedron axis makes a small angle with the (unit cell) cube axis. In the β-class the octahedron is found to be perfectly regular (at least in the Al^{+3} alums), its axes coinciding with the cube axis. About the γ-class, of which the only representative is sodium sulphate alum, no information is available regarding orientations. Though the Al^{+3} alums containing K, NH_4, Rb and Tl belong to α-class, and those containing Cs and NH_3CH_3 to the β-class (Beevers and Lipson, 1935; Klug, 1940), on changing over to Cr^{+3} alums both those containing Rb and Tl (almost of similar ionic radius) go over to the β-class. Rb seems to grow in both α and β classes and therefore is a link between the two. All these refer to SO_4, alums at room temperaperature.

(*c*) *Crystalline electric fields in the Cr^{+3} alums.*

Siegert (1936), Van-Vleck (1939), and Broer (1942) have postulated the existence of a predominantly cubic field, with a small superimposed trigonal field in all the alums. Though the X-ray structure of the β-alums seems to indicate a regular octahedron of water molecules about the Cr^{+3} ion, the adiabatic demagnetisation, paramagnetic absorption and resonance experiments all indicate a small separation of the spin levels and Van-Vleck (1939) has shown that a separation of this order arises with a distortion of the water octahedron by as little as $\sim 10^{-10}$ cm, which is below the margin of errors in X-ray measurements. Under the influence of the cubic field with a positive sign, as exists about the octahedrally coordinated Cr^{+3} ion in the alums (Gorter, 1932), the ground $3d^3\ {}^4F_{3/2}$-state of the Cr^{+3} ion splits up into an orbital singlet and two orbitals triplets above it separated from one another to the order of 10^4 cm^{-1}. Each triplet under the influence of the uniaxial field and spin orbit coupling breaks up into two sublevels separated to $\sim 10^{+2}$ cm^{-1} and 10^{+3} cm^{-1}. Of the four-fold spin degeneracy, only two-fold is removed to $\sim 10^{-2}$ cm^{-1} by the asymmetric field and the spin-orbit coupling λ, the other two-fold being of the Kramers' type remains unaffected by the crystalline field, unless magnetic, exchange or other types of interaction intervene.

The principal susceptibilities of the Cr^{+3} are given by Schlapp and Penney (1932); Abragam and Pryce (1951), Griffith and Owen (1952) as:

$$K_i = \frac{15N\beta^2}{12kT} g_i^2 \left\{1 - \frac{12}{5} \cdot \frac{X_i}{3kT}\right\} - 15N\beta^2\alpha_i \qquad \ldots (4)$$

in which the splitting factor $g_i = 2\gamma(1+4\lambda\alpha_i)$, α_i is a crystalline field constant used by Schlapp and Penney, i denotes either $\parallel$ (parallel) or $\perp$ (perpendicular) to the triagonal axis, $\gamma = 1.00115$ (Owen, 1955) the anomaly factor of the magnetic moment of electron (Kusch *et al*, 1952).

$$X_{\parallel} = 4\lambda^2(\alpha_{\parallel} - \alpha_{\perp}), \quad X_{\perp} = -2\lambda^2(\delta(\alpha_{\parallel} - \alpha_{\perp})$$

Then the square of the mean effective moment for the Cr^{+3} ion is obtained as:

$$p_f^2 = \frac{3kT}{N\beta^2}\left(\frac{K_{\parallel} + 2K_{\perp}}{3}\right),$$

$$= 15\left(\frac{g^2}{4\gamma^2} - 3kT\alpha - \frac{128}{15}\frac{\lambda^3}{kT}\left\{(\alpha_{\parallel} - \alpha_{\perp})^2\right\}\right) \qquad (5)$$

(neglecting the terms of the order of $\lambda^4\alpha^3$), in which

$$\alpha = \frac{1}{3}(\alpha_{\parallel} + 2\alpha_{\perp}), \text{ and} \qquad \ldots (6)$$

$$g^2 = \frac{1}{3}(g_{\parallel}^2 + 2g_{\perp}^2) = 4\gamma^2(1+4\lambda\alpha)^2 \qquad \ldots (7)$$

The first term in equation (5) is the Curie terms containing the contributions from the spin moment and from the orbital moment due to admixture of the upper orbital levels with the lowest, through spin-orbit coupling, the second term is the high frequency term of Van Vleck (1932) and the third arises from interaction of the spin levels with the orbital.

Equation (5) is equivalent to an experimental three-constant formula (3c) if we take:

$$A = -45k\alpha \qquad \ldots (8)$$

$$B = +\frac{15}{4\gamma^2} g^2 \qquad \ldots (9)$$

$$C = -128\frac{\lambda^3}{k}(\alpha_{\parallel} - \alpha_{\perp})^2 \qquad \ldots (10)$$

and the values of the three unknown quantities λ, α and $\alpha_{\parallel} - \alpha_{\perp}$ in the theoretical equation may be found out approximately from the above three equations, from the experimental values of A, B and C, if the results can be so represented.

We may try to ascertain whether the last term in equation (4) is sufficiently important to contribute any experimentally appreciable C term. The values of λ for the free Cr^{+3} ion is $+87$ cm^{-1} (Laporte, 1928) and this is probably not appreciably different from that in the solid state as will be discussed later. The value of $\alpha_{||} - \alpha_{\perp}$ could have been accurately known if an anisotropic class of Cr^{+3} salts similarly constituted as the alums could be measured. This being not the case we have used the value of $\alpha_{||} - \alpha_{\perp}$, obtained from the recent very accurate anisotropy measurements on $NiSO_4$, $6H_2O$ by Datta (1954), which should not be very different from that for Cr^{+3} alums, in view of the similarity in the Stark pattern for Ni^{+2} and Cr^{+3} ions. The value of $\alpha_{||} - \alpha_{\perp}$ for Ni^{+2} ion, is obtained from,

$$K_{\perp} - K_{||} = \frac{8N\beta^2}{3kT}\left(8\lambda - 3kT - \frac{2\lambda^2}{kT}\right)(\alpha_{\perp} - \alpha_{||}) \qquad (11)$$

to a fairly good degree of approximation (Schlapp and Penney, 1932), in which $\lambda = -335$ cm^{-1} (Laporte, 1928), $K_{\perp} - K_{||} = 348 \times 10^{-6}$ c.g.s.e.m.u. at 300°K (Datta. 1954), so that, $\alpha_{||} - \alpha_{\perp} \simeq +24.0 \times 10^{-6}$

Since in equation (9) the last term, $(\alpha_{||} - \alpha_{\perp})^2$ is involved, the sign of $\alpha_{||} - \alpha_{\perp}$ will not matter though this is evidently $-$ve in Cr^{+3} alums (Van Vleck, 1939). The magnitude may also be somewhat different but since the term is small, a rough estimate will be enough for our purpose. We then find for Cr^{+3}, the value of this term to be 2.3×10^{-4} at 300°K and 7.0×10^{-4} at 100°K, which is much smaller than the magnitude of errors in our experimental values. The Curie temperature corresponding to this term in equation (5) is ~ 0.005°K which is of about the same order of magnitude as .004°K (Leiden, 1949) and .011°K (Oxford, 1954) for Cr^{+3} alum found by adiabatic demagnetisation. It is interesting to note that if this term has been appreciable compared to other terms in equation (5) in the alums, we could have calculated $\alpha_{||} - \alpha_{\perp}$ the anisotropic field constant from equation (10), referring to even the mean square moments. Since we are justified in neglecting this term in equation (5) in our temperature range, arising from the theory in case of Cr^{+3} alums, if from susceptibility measurements a C term be still found to exist in the experimental results it must then be ascribed mainly to variations in g and α in equation (5) with temperature caused by thermal expansion of the alum lattice. This thermal expansion of the lattice directly affects very little the octahedron of water molecules immediately surrounding and firmly bound to the Cr^{+3} ion, but may considerably change the positions of the atoms outside the octahedron and thus indirectly affect the field due to the octahedron appreciably (Van Vleck, 1939; Bose, Mitra and Datta unpublished; Bose and Mitra, 1951). Indeed, as has been earlier noted, in the present case the thermal variations of g and α are of such a nature that instead of using a C/T term, the experimental data have to be represented in two-constant

form with different values $(A_1, B_1), (A_2, B_2)$ above and below the singularity region found to occur more or less continuously between 220°K and 160°K in most cases. In three cases one single two-constant formula is found to hold good over the entire range showing that the thermal variation of g and α is negligible.

Using the experimental values of B_1 and B_2 it is possible to calculate g' and g'', the values of the mean splitting factor g in the two temperature ranges, with a high degree of accuracy from equation (9). The high frequency term A has been predicted by Van Vleck (1932) to arise from the non-diagonal matrix elements of the magnetic moment corresponding to transitions to the upper levels, but was neglected in the treatment of Schlapp and Penney (1932), for Cr^{+3} ion to suit the earlier results of de Hass and Gorter. But we find that in many cases this term is quite appreciable, and has a positive sign. This is to be expected since in equation (8) α should have a negative sign for octahedrally coordinated Cr^{+3} ion (Van Vleck 1932, Gorter, 1932) and its magnitude is not very far from that of $NiSO_4$, $6H_2O$ (Mookherji, 1946) namely -8×10^{-5} cm. It will be seen that in several cases the h.f. term tends to become practically zero or even negative, especially on passing to the low temperature region. Though in such cases a part of this anomaly may be due to the large errors in estimating this term and also, to a small extent the diamagnetic corrections, the major part of this must be ascribed to other reasons to be explained in the later sections.

(*d*) *The splitting factor g in Cr^{+3} alums.*

It will be seen that in all the chrome alums the values of g are always less than $2\gamma(=2.0023)$ in both the high and low temperature ranges. This is always as it should be since in the formula $g = 2.0023\,(1+4\lambda\alpha)$, λ is positive and α is negative. It is to be remarked that in all the cases, except NH_2OH alum, g has appreciably higher value in the low temperature range, and in two cases, e.g. Tl sulphate and K sulphato-selenate, it approaches to within about 0.7 % of the spin only value. It should be seen that in these last two cases the high frequency term has a negative value in the *low* temperature range which according to (8) should have been positive. This negative value then indicates that g value is probably still varying with temperature in this range in such a direction as to mask the +ve value of the high frequency term and which hence may not be the true values independent of temperature. Indeed, one should regard with caution the absolute values of g and also of the h.f. term in such cases. The anomalous change of g in the NH_2OH alum, i.e. a decrease in the low temperature region, is also presumably to be ascribed to a similar reason, since the high frequency term in the high temperature range is found to be abnormally low and that in the low temperature range is also not very accurately determined. The negative and unusally small positive values of the high frequency term in several cases e.g. NH_4 sulphate, Rb sulphato-selenate in the low temperature range and NH_4 selenate also no doubt suffer from similar masking of the term. The general increase of g in all other cases on passing

from high to low temperature range, is indicative of the fact that α decreases more or less quickly from α' to α'' while passing through the intermediate temperature range indicated earlier; since it is not probable that λ can decrease with temperature.

TABLE XIII

Double sulphate series

	K	NH_4	Rb	Cs	Tl	NH_2OH
$A_1 \times 10^4$	18.5	5.0	10.2	8.0	10.0	0.0
B_1	14.36	14.29	14.49	14.40	14.22	14.68
g'	1.960	1.954	1.968	1.962	1.952	1.980
$-\alpha' \times 10^5$	6.03	6.8	4.90	5.70	7.1	3.45
in cms.	(6.0)	(2.0)	(3.3)	(2.7)	(3.2)	(0.0)
$A_2 \times 10^4$	12.5	−5.0	10.2	8.0	−15.4	16.0
B_2	14.66	14.61	14.49	14.40	14.77	14.65
g''	1.979	1.975	1.968	1.962	1.987	1.978
$-\alpha'' \times 10^5$	3.3	4.0	4.90	5.70	2.2	3.2
in cms.	(4.0)	(-ve)	(3.3)	(2.7)	(-ve)	5.0)

	(SO_4) (SeO_4) series				$(SeO_4)_2$ series	
	K	NH_4	Rb	Cs	NH^4	Rb
$A_1 \times 10^4$	10.2	12.0	12.5	12.5	1.1	6.45
B_1	14.56	14.31	14.30	14.30	14.48	14.53
g'	1.973	1.956	1.955	1.955	1.968	1.970
$-\alpha' \times 10^5$	4.2	6.60	6.75	6.75	4.90	4.60
in cms.	(3.3)	(3.9)	(4.0)	(4.0)	(1.2)	(2.4)
$A_2 \times 10^4$	−1.7	10.0	0.0	10.0	0.0	6.45
B_2	14.80	14.59	14.56	14.49	14.55	14.53
g''	1.988	1.974	1.973	1.968	1.972	1.970
$-\alpha'' \times 10^5$	2.85	4.02	4.2	4.9	4.33	4.60
in cms.	(-ve)	(3.2)	(0.0)	(3.2)	(0.0)	(2.4)

In the few cases, e.g. Rb, Cs sulphates and Rb selenate no change in g is observed over the entire range and the g values are very close to each other showing that they not only belong to the same class of alums but the crystalline fields in them are also very nearly the same and are practically constant in the entire temperature range. Rb and Cs sulphato-selenates though showing a considerable change

in g values in passing through the medium temperature range, have g values in the low temperature region very close to the previous three salts and to K sulphato-selenate and NH_4 selenate in the high temperature region and hence all these may be supposed to belong to the same class, in the respective range of temperatures [*class* (1)]. K, NH_4 and Tl sulphates NH_4, Rb and Cs sulphato-selenates, all at the high temperatures have distinctly smaller g values than the previous salts. The g's as also the high frequency terms being very similar, these alums should have similar crystalline fields (varying similarly with temperature) and belong to *class* (2). Apparently, K, NH_4, NH_2OH sulphates, NH_4 sulphato-selenate and NH_4 selenate have g values at low temperatures very close to each other and belong to *class* (3), but the high frequency terms in NH_4 sulphate and selenate are anomalous, and small changes in g values may have to be made on extending the temperature range. Tl sulphate and K sulphato-selenate at low temperatures have also negative high frequency terms and the high g values in them may have to be similarly even more reduced so that they may also be put amongst the last class. NH_2OH sulphate in high temperature range, for a similar reason belongs to *class* (1).

It would be worthwhile to compare our g values with the resonance experiments in this connection. Unfortunately the available data are given to be same for all sulphate salts $= 1.98 \pm .02$ (Bleaney, Bagguley and Griffith, 1951) so that the margin of error covers our observed variations of g. On the other hand, the nature of spin splitting from these measurements is appreciably different for the two classes of alums (Bleaney, 1951), (*a*) Rb, Cs, NH_3CH_3 alums having spin separations 0.165 cm^{-1}, 0.145 cm^{-1}, 0.165 cm^{-1} at room temperature show only very little decrease in the splittings which become practically constant below 90°K, (*b*) K and NH_4 alums have values near 0.12 cm^{-1} and 0.135 cm^{-1} at room temperature, but these splittings change enormously and in a complicated manner with temperature, falling to 0.055 cm^{-1} and 0.035 cm^{-1} near about 90°K, after which some sort of transition occurs and the salts consistently show an increased double value for the spin splitting about (0.32 cm^{-1}, 0.24 cm^{-1}) and (0.27 cm^{-1}, 0.15 cm^{-1}) for NH_4 and K alums respectively down to 20°K. The salts after transition are put in class (*c*) by Bleaney. The transition phenomena is similar to the findings of Kraus and Nutting (1941) from the studies of absorption spectra, though the classification of the alums from this and resonance measurements do not agree well.

It will be found from a consideration of our g values that our class (2) of alums having the largest departure of g from spin only value is identical with the class (*b*) of Bleaney (1951) and α class of Klug (1940). Our class (1) having a moderate departure of g value from spin only value is the same as the class (*a*) of Bleaney (1951) and β alums of Klug (1940). Our class (3) to which belong NH_4, NH_2OH, Tl sulphate and K and NH_4 sulphate-selenate, NH_4 selenate at low temperature has the highest value of g.

The considerable narrowing of the spin spliting in K and NH_4 sulphate alums in the range 300°K and 90°K shows that the anisotropic crystalline field is decreasing very much. The change in the anisotropic field with temperature may concievably be accompanied by changes in the average value of the field and hence of g as observed by us in these and similar alums. The spin splittings change very little in Rb and Cs sulphate alums in which we correspondingly find no appreciable change in g. A recent accurate value of g ($= 1.976 \pm .002$) from paramagnetic resonance (Bleaney and Bowers, 1951) not bound in the light refers to the K selenate alums diluted to 5 % concentration with Al-K selenate alum, and the temperature is not given but it seems to have about the g value as our class (1) alums.

The double splittings observed by the resonance experiments when class (2) of alums is cooled *below* 90°K, i.e. in class (c) of Bleaney, are probably due to coexistence in this region of two crystal phases of different space groups but of the same composition and cubic crystal class as the alums. The large changes in spin splittings (Bleaney, 1951) and in g values of this class *above* 90°K i.e. our class (2), observed by us as mentioned above are then no doubt precursors of the actual transitions to class (c) below this temperature. It is very probable that in all cases where we find a change of g value with temperature in our range, there is a continuous process of transition from $\alpha \rightarrow \beta$ or γ and $\beta \rightarrow \gamma$ phases of the alums. Apprently the electric fields are stronger in the β and γ alums since g values tend to increase towards the spin only value owing to greater quenching of the orbital moments. Further, during such a progressive change over, without change in the space group, taking place through a small rotation of the octahedral Cr^{+3} ionic group, as may quite possibly be due to anisotropic thermal expansion of the crystals, the magnetic properties may very well change in a continuous but non-linear manner as we observe. The irreversible tranisitions of Bleaney occur outside our temperature range, and in some cases do not probably take place at all even if it is near the bottom of our temperature range, since owing to methods of slow cooling of the specimen, strains set up are never enough to shatter our crystals as we observed and supercooling very probably takes place. In one case only, that of $(NH_4)_2SeO_4$ alum, a rather sharp and irreversible change has been observed in magnetic moment near about 106°K as will be found from the p_f^2 value at the bottom of the temperature range given in Table XII. This is more or less in agreement with Kraus and Nutting's ovservation.

(*e*) *Calculation of the spin-orbit coupling constant.*

From the equation :

$$\frac{p_1^2 - n^2}{} \quad \frac{8\lambda - 3kT_1}{8\lambda - 3kT_2} \qquad \ldots (12)$$

(derived from equation 5, neglecting the terms involving $\lambda^2\alpha^2$, and $\lambda^3(\alpha_{\parallel} - \alpha_{\perp})^2$ which are very small) *i. e.* the ratio of the excess of the p_f^2 over the spin only

value at two extreme temperatures, for any given alum, eliminating α, taking to to be constant, we may calculate the value of λ. In view of (1) the small value of the above excess, (2) the uncertainty in the high frequency term due to changes in g with temperature in many cases (3) the fact that α is not constant, also (4) that in the medium temperature range the temperature variations can not be made to fit with the theoretical formula, the calculation of λ has to be done preferably from the rather limited upper range of temperatures; the value of $\lambda \approx +100$ cm^{-1} for K, Rb, Cs salts so calculated is to be considered satisfactory.

A slightly better way of calculation is from the g value from which α is eliminated using (Eq. 7), since this gives due weight to all the experimental points in the given temperature range. Of course the values g' and α' in the upper range should be used here also. λ comes out to be between $+54$ and $+120$ cm^{-1} for most of the salts, giving a mean value $+84$ cm^{-1} as against $+87$ cm^{-1} in the free ion. The differences between individual salts are due to uncertainties in the experimental determination of the g' and α' values, due to reasons already mentioned.

That λ should be more or less the same in the solid state and free ion has been verified by the measurement of Krishnan and Bose (1938), Bose, Mitra and Datta (unpublished); Bose (1948) for Ni^{+2} salts. Owen (1952) and Bleaney (1951) have recently shown from theoretical considerations that λ should be practically the same for the free ion value and in the solid state, though others (Van den Handel and Siegert, 1937; Abragam and Pryce, 1951; Griffiths and Owen, 1952) have claimed a decrease in λ as large as 30-40 % in the solid. It appears from these investigations that owing to a partial sharing of the $3d$ electrons of the central paramagnetic ion by the surrounding eight oxygen atoms of the water octahedron, both g and the high frequency terms are affected, so that these are really given by,

$$A = -45\ k.\alpha.f$$
$$g = 2\gamma(1+4\lambda\alpha.f),$$

instead of equations (8) and (7) where f is the 'covalency factor'.

Our calculation of λ (incidentally of Krishnan and Bose also) is then still valid and gives us the actual value of λ in the solid state (or for free ion), since what we have eliminated is really the *effective* value of the field constant, $\alpha_f = \alpha.f$ inclusive of the covalency factor f. The lower value of λ obtained by the other authors are due to their method of calculation which includes f in the value of λ.

(f) Calculation of the effective field constant and covalency factor

In view of the large errors in the calculation of α_f in many cases directly from the high frequency term, particularly in the low temperature region where several of these terms are abnormally small or even negative, it would be better to calculate them from the g value $= 2\gamma(1+4\lambda\alpha_f)$, where λ is known. From what has been

said in the earlier section, the value of λ calculated, suffers much from not only errors in the A and B terms but also from the variations in the value of α_f due to thermal expansion of the lattice and transitions from one phase to another. It would be then better to assume $\lambda = +87$ cm^{-1}, the free ion value in all cases. The values of α_f thus caclulated from g as also from high frequency term, where possible, are actually those given as α' and α'' in Table XIII. It would be seen for all the alums of NH_4 sulphate class, the α-class, the mean value of α_f is about 6.7 $\times 10^{-5}$ cm, for Rb sulphate class presumably the β-class, the mean value is about 5.0×10^{-5} cm, which are somewhat smaller than the value 8.0×10^{-5} cm in $NiSO_4$, $6H_2O$. For the last class to which belong K and NH_4 sulphates and several other alums at low temperature, the mean value is 3.5×10^{-5} cm. Very probably these values are much closer to each other perhaps about 6, 5.5, and 5.0 for the three classes respectively, in view of large uncertainty in the experimental values; and one has to be satisfied only with a qualitative discussion of the results. The values of α_f from h.f. terms where possible to estimate with sufficient certainty, also support this conclusion.

It is known from the theory of Owen (1952) that $-1/\alpha$ and $-1/7\alpha$ (in which α is the *actual* value of the field constant) are the separations of the mean centres of the lower and upper orbital triplets respectively, from the lowest singlet in the Stark pattern of Cr^{+3} alum. But since the values of α found from our measurements are the *effective* ones inclusive of the covalency factor what we obtain from these are only the effective separations. It would be worth while to compare these separations with the extensive optical absorption data on the Cr^{+3} alums by Kraus and Nutting (1941) and on Cr^{+3} chloride solutions by Tsuchida and Kobayashi (1938) quoted by Hartmann and Schlafer (1951). Their results differ considerably, the former giving near about 15000 cm^{-1} differing by a few hundred cm^{-1} at most from alum to alum, the latter 17500 cm^{-1}, as the first absorption level, of which evidently the former value is more appropriate to the present discussion on Cr^{+3} alums. Our mean *effective* separations for the three classes of alums corresponding to above absorption level are roughly about 16600, 18200 and 20000 cm^{-1} respectively. The ratio of the *actual* (optical) to *effective* separation gives us the shared $3d$ electrons of the Cr^{+3} ion spend correspondingly longer fractions of time in the σ orbitals (and possibly π orbitals also) of each of the oxygen atoms of the water octahedron for the three classes. The value quoted by Owen for this is 0.6 calculated from the g value for highly diluted Cr^{+3} selenate alum, 1.976 given by resonance method (Bleaney and Bowers, 1951), and Hartmann and Schlafer's value of actual separation for Cr^{+3} chloride solution (which is normally a green solution in which the Cr^{+3} complex constitution is surely different from the alums). Our values show that in the alums the covalency factor is probably larger than estimated by Owen, i.e. the bonds are more ionic. The mean centre of the upper level taking these values of f comes out to be at about 21000 cm^{-1}, as the mean for the three classes, but for this, data are not available for Cr^{+3} alums, and for

thec hloride solution mentioned the value is 24500 cm^{-1}. The difference from the mean value for the individual salts indicate, though qualitatively, the differences in "actual" crystalline field in them. The differences arise evidently from the variation in the long range structures of the alums, due to replacement of one monovalent cation or diavalent anion by others and by the disturbing influence of the temperature, and their indirect action on the size and shape of the (Cr^{+3}, 6 H_2O) octahedron, according to the theory of Van Vleck (1939).

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